Comment on "Effects of hydrogen dilution on deposition process of nano-crystalline silicon film by $SiCl_4/H_2$ plasma". [J. Phys. D: Appl. Phys. 39 (2006) 3030]

Isabel Tanarro

Inst. de Estructura de la Materia, CSIC, Serrano 123, 28006 Madrid, Spain.

In a recent work [1] Wang et al. have reported the effects of hydrogen dilution ratio on the relative densities of $SiCl_n$ (n = 0–2) radicals in a $SiCl_4/H_2$ plasma generated in a RF low pressure discharge. Measurements of radical concentrations are attempted by means of quadrupole mass spectrometry with ionization by electron impact. The differentially pumped mass spectrometer is connected to the plasma through a narrow and relatively long tube, and the radical detection technique employed is the so called "straight line fit method", previously proposed by the same authors [2] to determine in a SiH_4 discharge the depletion fraction, f, of the precursor, i.e. "the ratio of dissociated and ionized precursor molecules to all precursor molecules in the plasma with the discharge off". Relative concentrations of SiH_n (n=0-3) radicals were estimated in ref. [2] with the same procedure.

The aim of this comment is to show that the proposed method is not appropriate to estimate radical concentrations. Therefore, the experimental results obtained with it seem unreliable.

To estimate the precursors' depletion fractions of $SiCl_4$ [1] and SiH_4 [2] in the respective plasmas, the authors measure the amplitude changes with discharge on, S^n_{on}, and discharge off, S^n_{off}, of peaks of their mass fragmentation pattern at m/q^+ ratios corresponding to those of the respective radicals ($SiCl_n$ (n=0-2) [1] and SiH_n (n=0-3) [2]). With discharge on, the S^n_{on} value given by the mass spectrometer includes the signal corresponding to dissociative ionization of the precursor, whose concentration is depleted by dissociation in

the plasma and conversion to another products, and the signal corresponding to direct ionization of the daughter radical generated in the plasma, S^n, in such a way that:

$$S_{on}^n = S^n + (1-f)\cdot S_{off}^n \qquad (1)$$

S_{on}^n and S_{off}^n intensities are measured for different electron impact ionization energies, E_e = (25 - 100) eV, and compared with the corresponding theoretical ionization cross sections values $\sigma_n\ (E_e)$ of these radicals, taken from the literature. This comparison is performed through a mathematical reasoning which implies a linear dependence between two parameters, C_1^n, C_2^n, involving the experimental intensity values, with and without discharge, and the above mentioned theoretical cross sections:

$$C_2^n = \frac{S_{off}^n(E_e)}{\alpha_n(E_e)} \qquad (2)$$

$$C_1^n = \frac{S_{off}^n(E_e) - S_{on}^n(E_e)}{\alpha_n(E_e)} = -S_0^n + f\cdot C_2^n \qquad (3)$$

where $\alpha_n(E_e)$ is defined as

$$\alpha_n(E_e) = \sigma_n(E_e)/\sigma_{n\,max}(E_0^n) \qquad (4)$$

$\sigma_n(E_e)$ and $\sigma_{n\,max}(E_0^n)$ are the ionization cross section at the electron energy (E_e) and the maximum ionization cross section corresponding to a certain electron energy (E_0^n) for each $SiCl_n$ (n=0,2) [1] and SiH_n (n=0-3) [2] radical, respectively. S_n^0 is defined as the mass spectroscopic signal of $SiCl_n$ (n=0-2) [1] and SiH_n (n=0-3) [2] at the electron energy E_0^n corresponding to the maximum ionization cross section.

The slope, *f*, in equation (3) is just the depletion fraction [1]. It is worth mentioning that the usual procedure to estimate the depletion of the precursor in the plasma, which consists in comparing the peak corresponding to the parent molecule with discharge on and

off, is not employed in the mentioned works. This method is much simpler, requiring only a fixed E_e value and avoiding the need of additional cross section data. The limited mass range of the mass spectrometer (SRS RGA 100) up to 100 a.m.u prevents obviously the detection of the parent ion in the case of $SiCl_4$ [1], but not in the case for silane (ref [2]), although the peak corresponding to SiH_4 is not a major one in its fragmentation pattern [3].

Once the *f* value is obtained (with its inevitable experimental uncertainty), the authors use the expression

$$S^n(E_e) = S^n_{on}(E_e) - (1-f)\cdot S^n_{off}(E_e) \qquad (5)$$

quite similar to Eq. (1), to estimate the radical concentration, $S^n(E_e)$. Nevertheless, in order to do this, the authors employ the measured values of $S^n_{on}(E_e)$ and $S^n_{off}(E_e)$ at an electron energy of 90 eV, and they use this energy in spite of admitting [2] that "when the electron energy is in the range of 50-100 eV, several times the dissociative ionization threshold energy of the precursor, the contribution of $S^n(E_e)$ to $S^n_{on}(E_e)$ can be negligible".

Therefore, the method proposed in refs [1-2] to estimate radical concentrations is not valid. The problem arises from the fact that radical densities in reactive plasmas like $SiCl_4$ and SiH_4 are usually several orders of magnitude lower than the precursor density [4], their concentration depending inversely on their reactivity. At large electron energies, the signals detected with a mass spectrometer at a m/q^+ ratio corresponding to a given radical when discharge is on will correspond, almost exclusively, to the dissociative ionization of the precursor practically in an exclusive way. With the method proposed in refs. [1, 2], it is attempted to measure radical densities from a subtraction of two values, $S^n_{on}(E_e)$ and $(1-f)\cdot S^n_{off}(E_e)$, which are very close one to each other, in such a way that their respective experimental uncertainties are much larger than the difference between them.

A very well known alternative method to measure radical densities by quadrupole mass spectrometry with electron impact ionization, which is somehow similar to the present one but avoids the problems just commented on, is to use the "threshold ionization technique", also known as "appearance potential technique" [4-8]. This technique employs the fact that threshold energies for direct ionization of the radicals, e.g., $CH_3 + e^- \rightarrow CH_3^+ + 2e^-$, are usually two or more electronvolts lower than the threshold energies for the corresponding dissociative ionization of the mother molecules leading to the same ion, e.g., $CH_4 + e^- \rightarrow CH_3^+ + H + 2e^-$. During the measurement, the electron energy in the ionizer is varied in the region of these two thresholds. This allows discriminating the radical signal from the signal of stable neutrals that, as mentioned above, are usually much more abundant. The partial ionization cross sections necessary for the quantification are taken from the literature.

Last but not least, concerning the plasma sampling geometry by mass spectrometry employed in Refs. [1, 2], and given the high reactivity of the radicals to be detected, it is not possible to sample them reliably through a long and narrow tube because most of their concentrations disappear by reactions in gas phase or in the wall inside the tube, before reaching the mass spectrometer. A small diaphragm directly exposed to the plasma is placed usually between the plasma reactor and the differentially pumped mass spectrometer chamber [6,9], but a molecular beam modulated by a mechanical chopper, with one or more differentially pumped stages, is even employed frequently when the radicals' concentrations are extremely low [8,10].

Aknowledgment

IT acknowledges funding from MEC (Projects No. FTN-2003-08228-C03-03, FIS2004-00456 and ENE2006-14577-C04-03)

References

[1] Wang Z K, Lou Y H, Lin K X, Lin X Y, Huang R and Wei J H 2006 *J. Phys. D: Appl. Phys.* **39** 3030

[2] Wang Z K, Lin K X, Lin X Y, Qiu G M and Zhu Z S 2005 *Chin. Phys. Lett.* **22** 904

[3] NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

[4] Robertson R, Gallagher A 1986 *J. Appl. Phys.* **59** 3402

[5] Sugai H, Toyoda H, 1992 *J. Vac. Sci. Technol. A* **10** 1113

[6] Sanz M M, Abad L, Herrero V J, Tanarro I 1992 *J. Appl. Phys.* **71** 5372

[7] Tserepi A, Schwarzenbach W, Derouard J, Sadeghi N 1997 *J. Vac. Sci. Technol. A* **15**, 3120

[8] Singh H, Coburn J W, Graves D B 2000 *J. Vac. Sci. Technol. A* **18** 299

[9] Bauer M, Schwarz-Selinger T, Jacob W, von Keudell A 2005 *J. Appl. Phys.* **98** 073302

[10] Benedikt J, Eijkman D J, Vandamme W, Agarwal S, van de Sanden MCM 2005 *Chem. Phys. Lett.* **402** 37